Supporting information

Electron Transfer Reactions of Electronically Excited Zinc Tetraphenylporphyrin with Multinuclear Ruthenium Complexes

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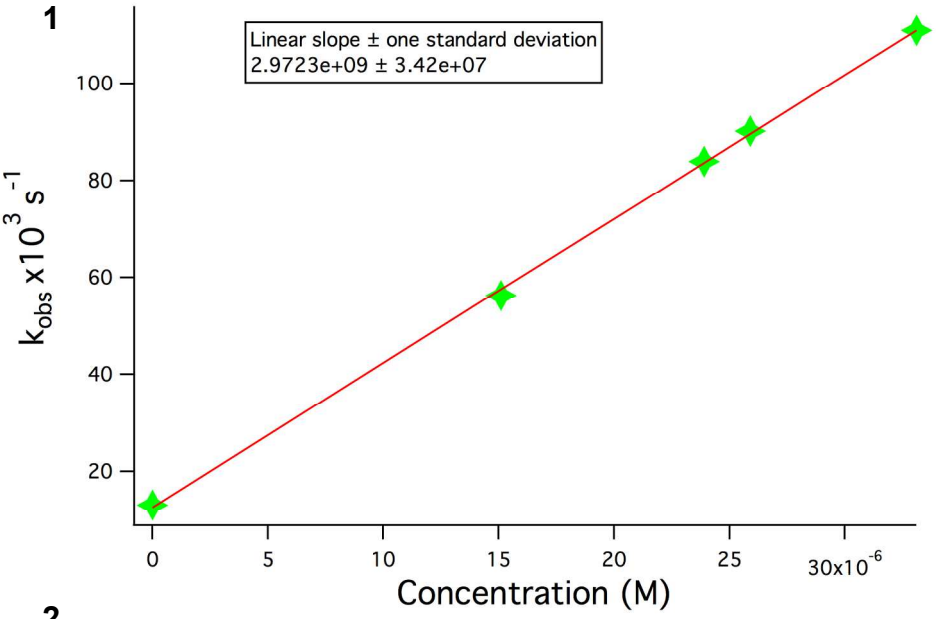

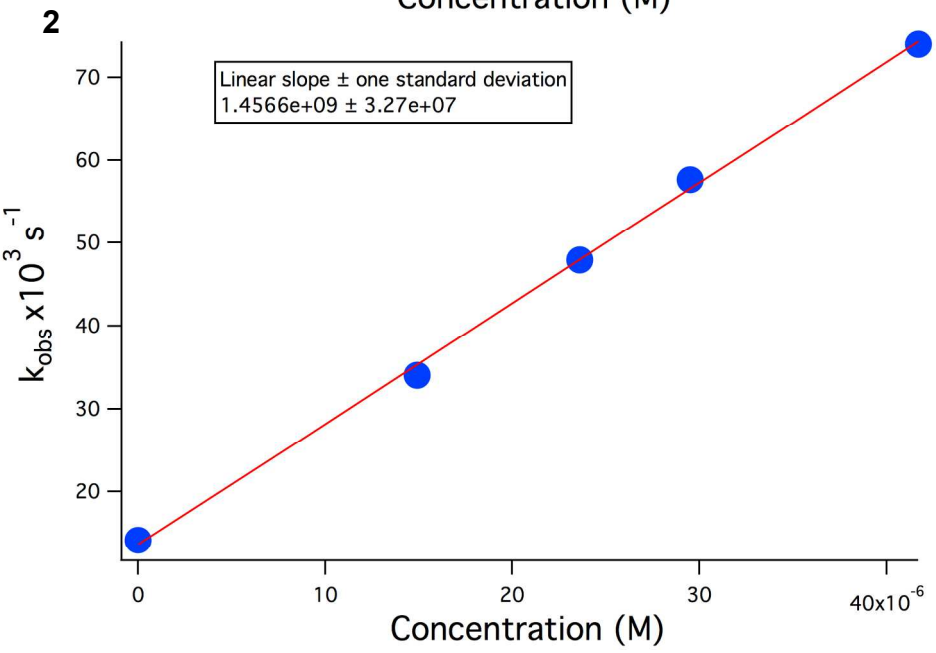

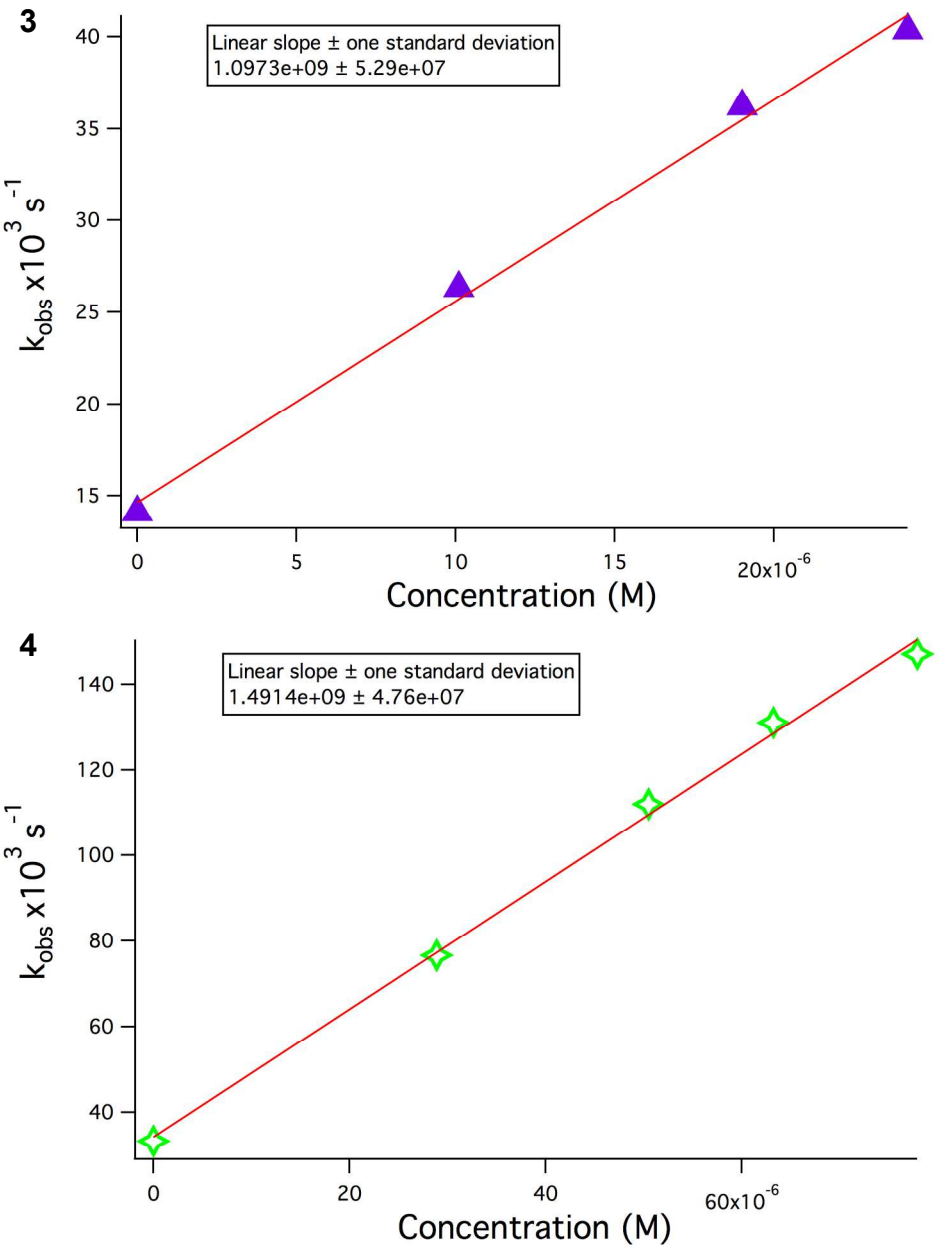
3
Linear slope ± one standard deviation
1.0973e+09 ± 5.29e+07
k_{obs} x10^3 s^{-1}
40
35
30
25
20
15
0
5
10
15
20x10^{-6}
Concentration (M)
4
Linear slope ± one standard deviation
1.4914e+09 ± 4.76e+07
k_{obs} x10^3 s^{-1}
140
120
100
80
60
40
0
20
40
60x10^{-6}
Concentration (M)

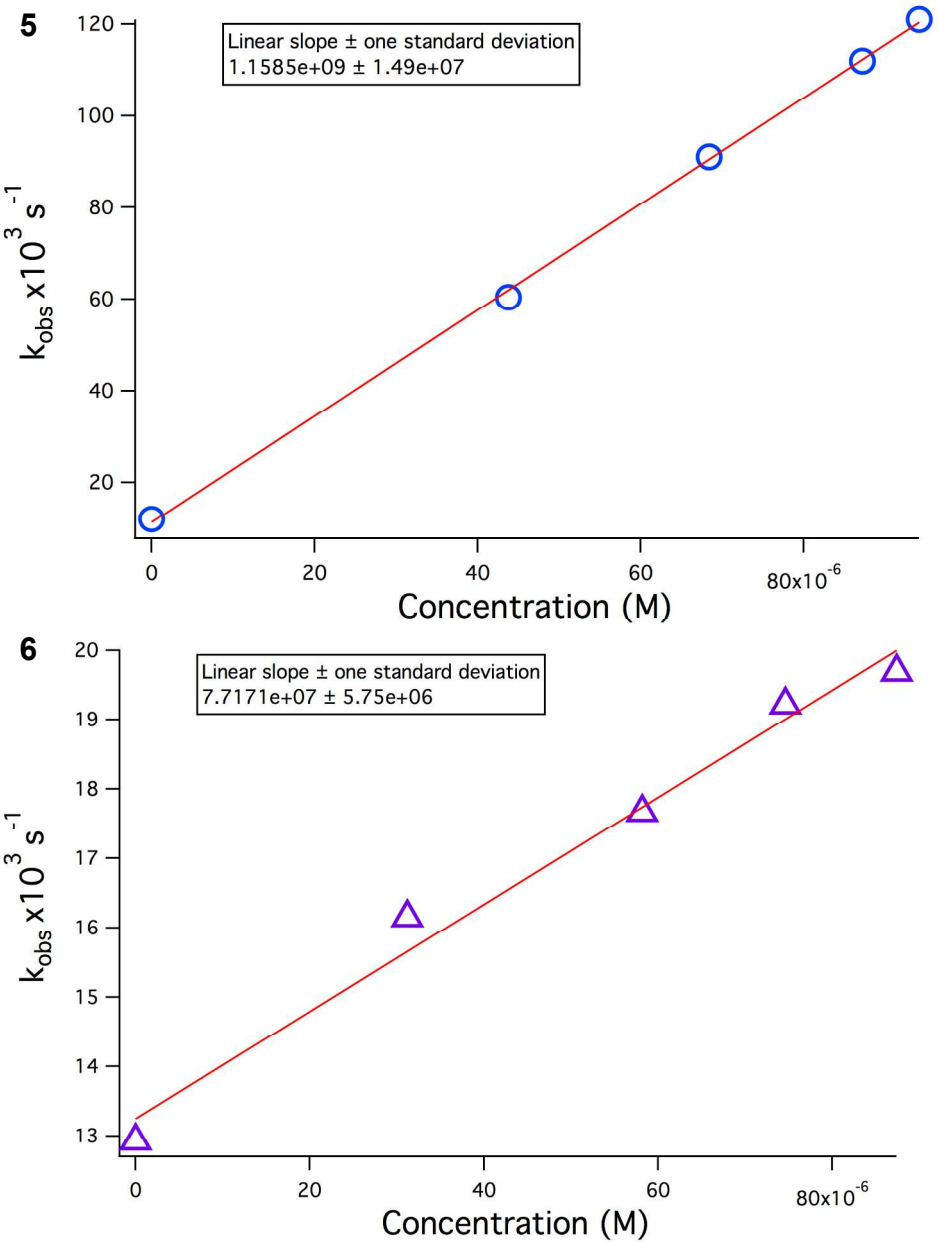

Figure S1. Linear dependence of the single exponential decay rate constant, k_{obs}, versus concentration for **1** – **6**. The bimolecular collisional quenching rate of ^{3}ZnTPP*, k_q, is derived from the slope of the linear fit.

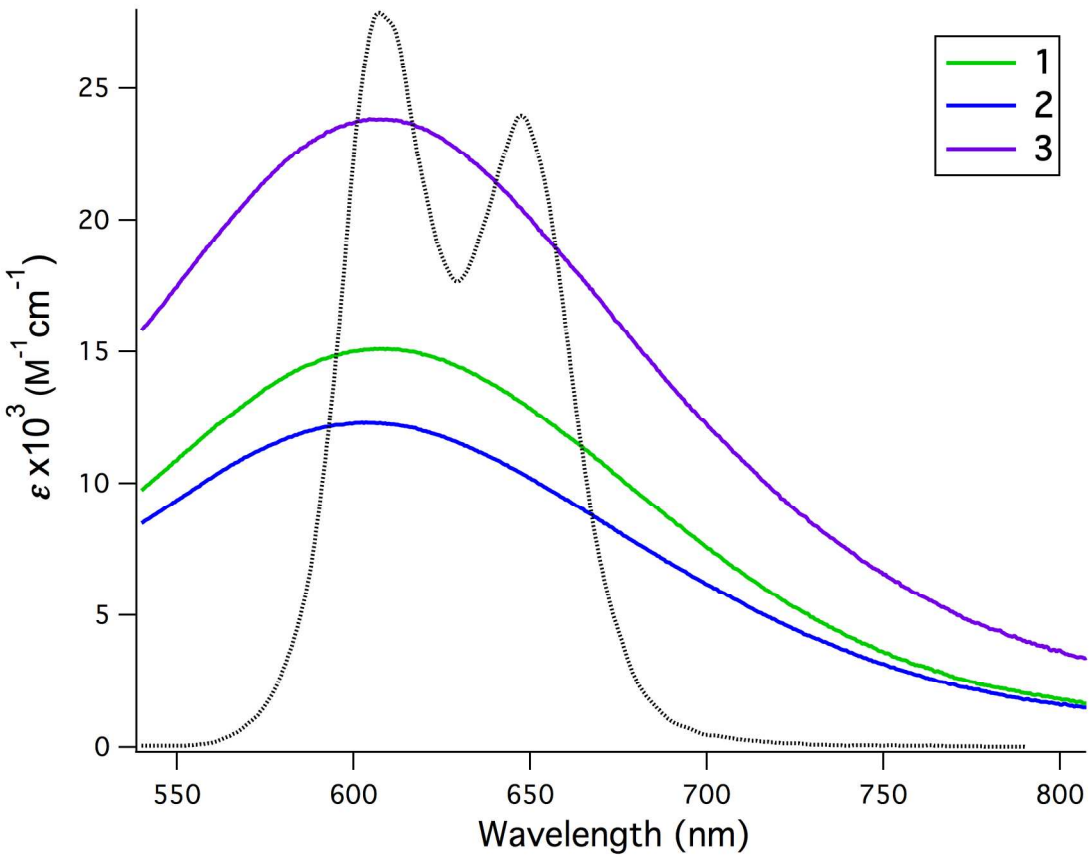

Figure S2. Fluorescence intensity of ZnTPP following excitation at 500 nm (grey trace) and electronic absorption of **1** – **3**.

Förster's Resonance Energy: overlap integral[1]

$$J(\lambda) = \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$$

The overlap integral expresses the degree of spectral overlap between the donor emission and the acceptor absorption. Here $F_D(\lambda)$ is the normalized fluorescence intensity of the donor in the wavelength range of λ to $\lambda + \Delta\lambda$ and $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor at λ.

As all other variables of the energy transfer rate constant expression remain unchanged across all samples, the Förster's distance R_0^6 (a function of $J(\lambda)$) predicts the rate of energy transfer would be greatest for **3** and lease for **2**, resulting from Figure S2.

$$k_T(r) = \frac{1}{\tau_D}\left(\frac{R_0}{r}\right)^6$$

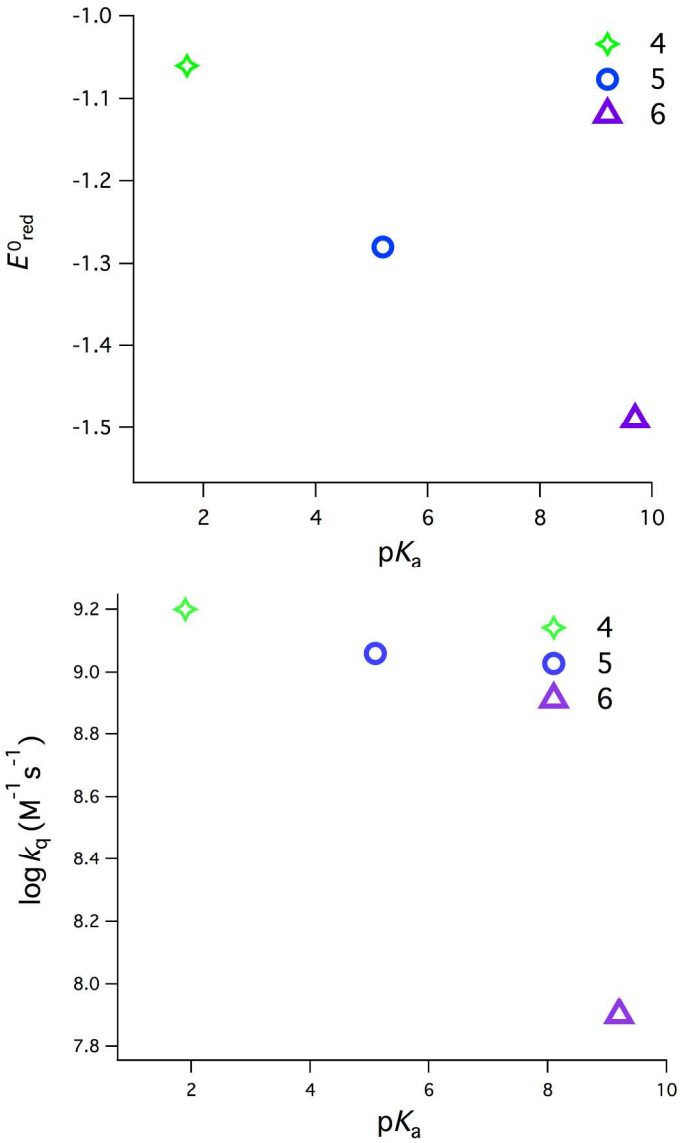

Figure S3. Ancillary ligand effect on electrochemical reduction (left) and quenching rate constant (right) for **4** – **6**. Correlation with pyridyl ligand electronics are described by respective pK_a values.

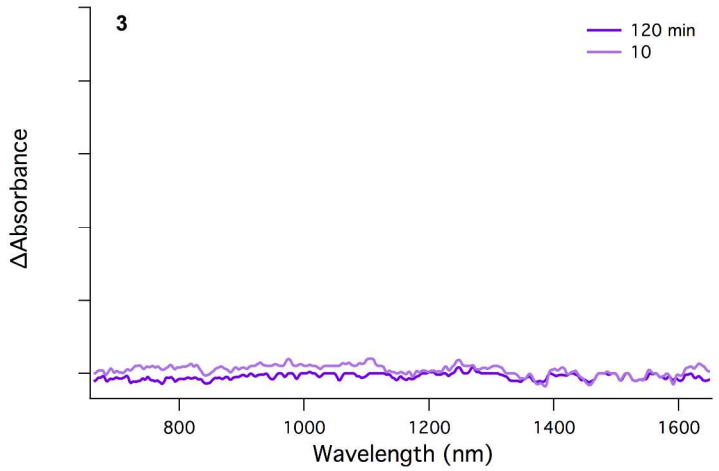

Figure S4. Difference near-IR absorbance of 50 μM **3** in CH_3CN solvent with 0.1 M $TBAPF_6$ and 0.50 mM sacrificial donor (BNAH) following photolysis with 568 nm light.

Alternative mechanism of Ru_3O-pz-Ru_3O reduction

It is possible that $^3ZnTPP^*$ may become reduced via a hole transfer to the sacrificial donor, generating a $ZnTPP^{-\bullet}$ radical anion. The reduction potential of ZnTPP is -1.7 V vs. Fc/Fc^+ and the resulting free energy change for an electron transfer from BNAH to $^3ZnTPP^*$ is 0.33 eV.[2] As the driving force for the initial reduction of $^3ZnTPP^*$ by BNAH is more positive than the driving force for the proposed initial reduction of Ru_3O-pz-Ru_3O by $^3ZnTPP^*$, the electron is predicted to be transferred from a neutral porphyrin. The driving force for BNAH to reduce the resulting porphyrin cation is negative, allowing the regeneration of the neutral ZnTPP to be thermodynamically favorable. Regardless of mechanism, the photolysis results show that it is thermodynamically possible to photochemically reduce dimers **1** and **2**, to form the desired mixed valence state.

References

(1) Lakowicz, J. R. *Principles of fluorescence spectroscopy*; 3rd ed.; Springer-Verlag: New York, NY, 2006.

(2) Göransson, E.; Boixel, J.; Monnereau, C.; Blart, E.; Pellegrin, Y.; Becker, H.-C.; Hammarström, L.; Odobel, F. *Inorg. Chem*. **2010**, *49*, 9823.